Numerical simulation of capture of diffusing particles in porous media

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Abstract. Numerical modeling of the capture of particles, diffusing in media with pores, on traps was carried out. The pores are cylindrical in shape and the traps are randomly distributed along the cylindrical surface of the pores. The dynamics of particle capture on traps and filling of traps have been studied. In general, the decrease of particles is exponential with a characteristic time determined by the concentration of traps. However, at long times extended plateaus of the distribution function appear. Further, we studied the dynamics of the interface boundary, corresponding to the median filling of traps M = 0.5, in other words, this interface separates the region where traps are filled with a probability greater than 0.5 from the region where traps are filled with a probability less than 0.5. The motion of the interface over time has been approximated by a logarithmic dependence on time. For the first time, the appearance of fluctuation regions - regions free from traps at long times - has been discovered, which in numerical modeling manifests itself in the form of steps in the particle distribution function due to the lack of capture by traps.

Keywords: diffusion, capture on traps, porous materials, numerical simulation.

1. INTRODUCTION

The problem of particle diffusion in media with absorbing traps has been studied in many works [1-5]. Interest is also due to the expected new features in particle transport [7-10], as well as various applications. One of the most relevant applications is the study of the processes of diffusion and capture of active particles into traps in porous dielectric low K materials [11-14].

In this paper, we investigate diffusion processes in porous media with traps, in particular, we investigate the decrease in the number of active particles over time due to capture by traps. Additionally, we establish the characteristic time dependence of traps capture on the traps concentration. As is known, in various physical phenomena, characteristic parameters usually arise that describe these phenomena. In the problem of diffusion processes in media with traps, a characteristic length arises – the distance between the traps and, accordingly, in dynamics, the diffusion time for a distance of the order of the length between the traps. In the one-dimensional case, it is equal to:

$$t_c = \frac{1}{Dc^2}$$

(1)

D - is the diffusion coefficient, c - is the traps concentration, in the one-dimensional case, the distance between traps is equal to the inverse concentration. Accordingly, different behaviors are possible at short $t << t_c$ and long times $t >> t_c$, which we described in the article.

The article constructs as follows. The second section formulates the problem, briefly describes the algorithms and methods of numerical modeling, and provides characteristics of the trap seeds. The third section presents the main results of the numerical experiment. The fourth section discusses the features of long-term asymptotic of the active particles survival probability. The Conclusion discusses the results.

2. PROBLEM STATEMENT. ALGORITHMS OF SIMULATION.

We consider the active particles diffusion in a cylindrical

$$N(x, t=0) = N_0$$

pore, the cylinder radius R and height H are specified during simulation. The traps are located randomly on the pore surface at different trap concentration degrees. Since the diffusion equation is a first-order equation in time, the diffusion processes dynamics is determined by the initial condition at the zero moment of time , when there are only N-particles with a uniform density and boundary condition at the top of the cylinder in the plane $Z = 0$. This formulation corresponds to the propagation of free oxygen, we call O-particles, in the pores of the material in which traps - C particles - are randomly located. A similar problem was considered in [15], but there a one-dimensional approximation with three types of particles was used (bound oxygen was additionally taken into account). In the present work, a three-dimensional geometry is used - the pores of the material in the form of a cylinder, which is more consistent with the geometry of low k materials.

2.1. Algorithm of simulations. Diffusion processes in media with traps.

Let us briefly describe the modeling particle diffusion algorithm in cylindrical pores with traps on surfaces of cylinder. A random number generator chooses the direction of particle movement arbitrarily at every step, it simulates random motion of particle. In this case, there are number of conditions: a) after choosing the direction of movement, the algorithm checked whether there is a particle in the new coordinate, if the coordinate is "free" the particle moves to it, otherwise it remains in its place. b) upon reaching the lower or upper boundary of the cylinder, the particles are "reflected", that is, they return to their original position. c) the cylindrical surface is reached when the distance from the center of the circle on the cut along the z coordinate exceeds the radius of the cylinder. In this case,

"reflection" occurs. We used the "Mersenne Twister (MT19937)" algorithm to generate random numbers.

2.2. Placing of traps.

During diffusion particles are captured on traps, which placed on the surface of cylinder pores. Coordinates of traps are determined by random way, namely: the Z coordinate selects randomly – the height of the location on the axis of the cylinder, then it randomly select angle and calculates the X and Y coordinates. The obtained coordinates rounded to an integer value by discarding the fractional part. Thus, the traps form a "belt" around the working area.

3. MODELLING PROCESS AND RESULTS OF NUMERICAL SIMULATION.

To simulate diffusion, we generate various trap configurations, with the number of traps varying from 1000 to 10000 in 1000 increments. Data of the active particles number were recorded every for every 1000 iterations for all generated traps configurations. The resulting data on the configurations were averaged and a graph of the change in the active particles number from the number of iterations was constructed - see Fig. 1.

Figure 1

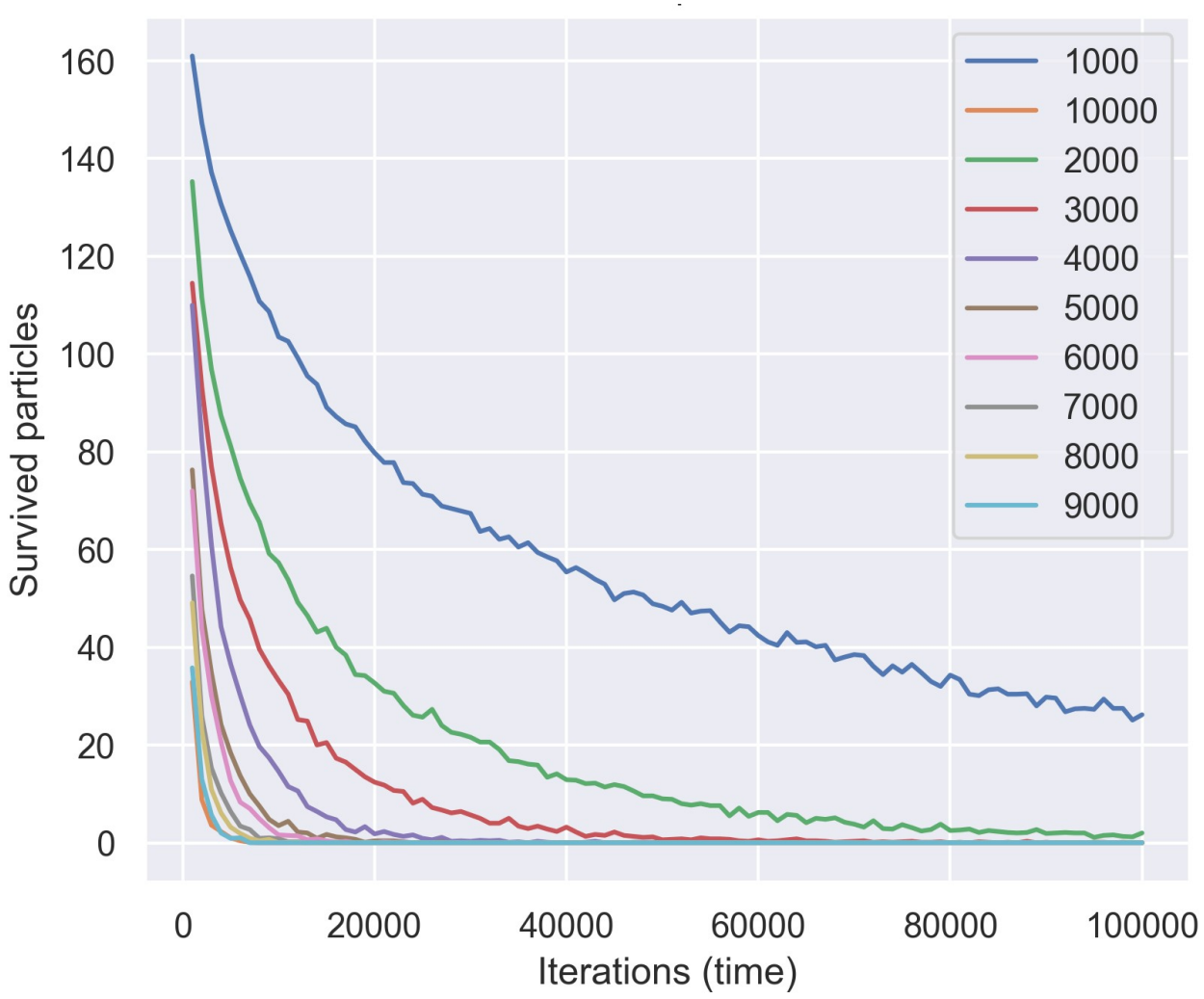

Fig.1 Dependence of number of survived particles on the time (iterations) at different number of traps.

It is obviously that there is a sharp decreasing of number of survived particles with increasing number of traps. So let's use the logarithm scale for a number of survived particles at different concentrations of traps at the insert at Fig.1.

Figure 2

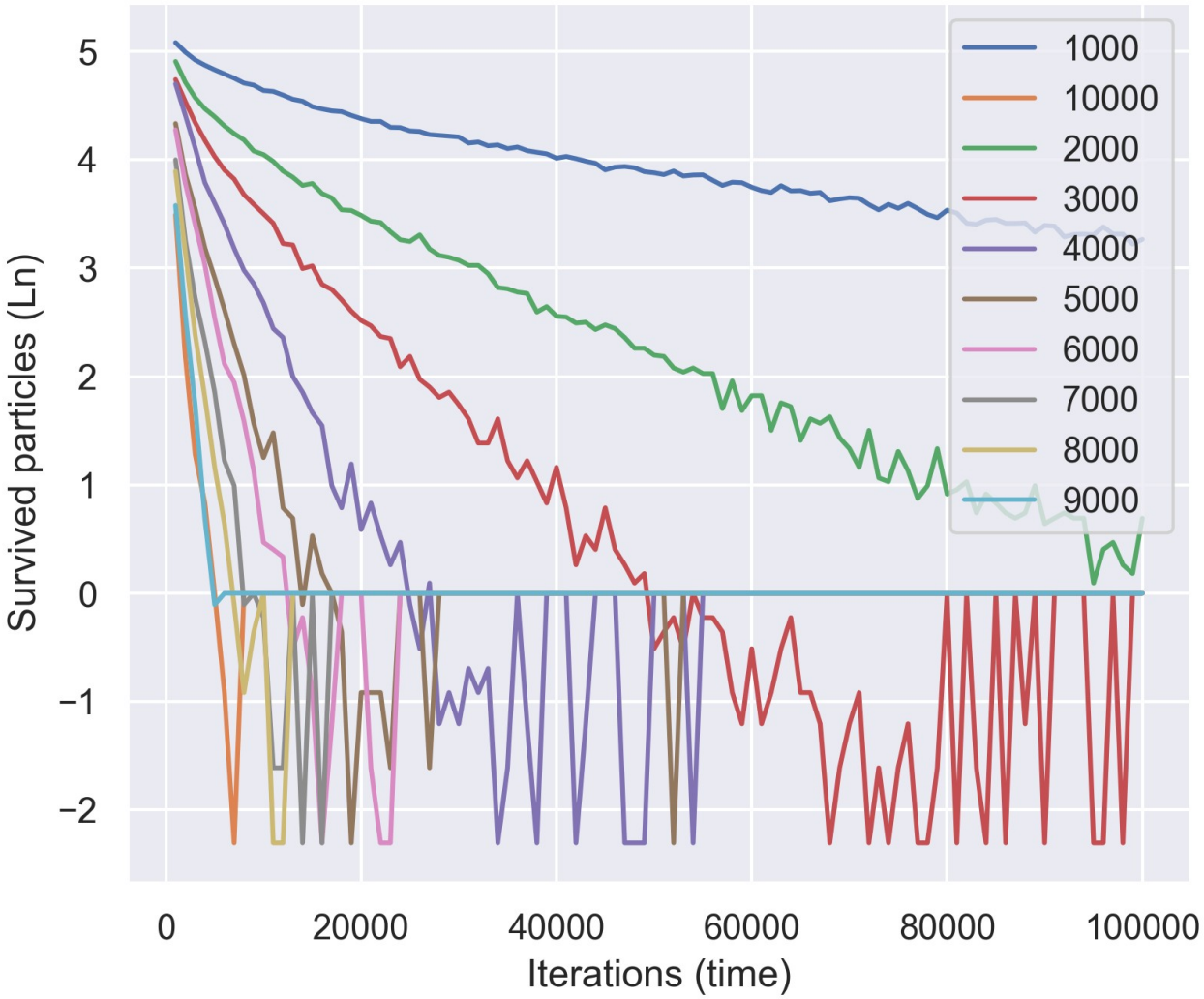

Fig.2. Dependence of logarithm of number of active particles on time at different concentrations of traps.

For a more complete description of the processes of capture of diffusing particles on traps, we will calculate some characteristics of these processes.

3.1. Motion of the interface of the region with median filling of traps.

In addition to the surviving particles, the coordinates of the closed traps are recorded during the numerical simulation. Let us consider the moduli of the Z coordinate for each of the closed traps.

Distribution at Z

First, let's consider the distribution of closed traps along the Z axis. For each time step (each iteration), we obtain an array of pairs - (Z value and number of closed traps). We can describe these data as a map object where key is Z coordinate, and value is the number of traps. The mean and median values can be used as characteristics of this array. Table 1 presents example of medians and means for closed traps data of numerical simulation with traps $N_t = 1000$.

Table 1. The average and median value of the z coordinate for closed traps (configuration with the number of traps 1000)

№	Number of steps (number of iterations)	Median value	Mean value
1	1000	23,4	21,705
2	5000	32,0	36,494
3	10000	43,0	46,680
4	20000	50,0	58,322
5	30000	64,0	66,022
6	40000	67,0	67,367
7	50000	75,0	74,778
8	60000	80,0	81,345
9	70000	75,0	74,556
10	80000	81,0	81,934
11	90000	85,5	84,524
12	100000	88,5	89,394

The results have a clear sense: as the more time steps (iterations), then the more traps are “closed” and, as a result, the “shift” of the median and average coordinate value occurs.

Median and average

Let us consider how the median and average value of the boundary separating the areas with trap filling greater than 50% from the area with less filling changes over time (number of iterations) for different trap concentrations. For each trap concentration, the average and median values for the Z coordinates of closed traps, as well as the total number of closed traps, were calculated. Thus, for each numerical experiment, the average by coordinates, the median by coordinates, and the number of closed (knocked out) traps were obtained.
The general graph of the change in the average value of the interface position from the number of iterations is shown at Figure 3.

Figure 3

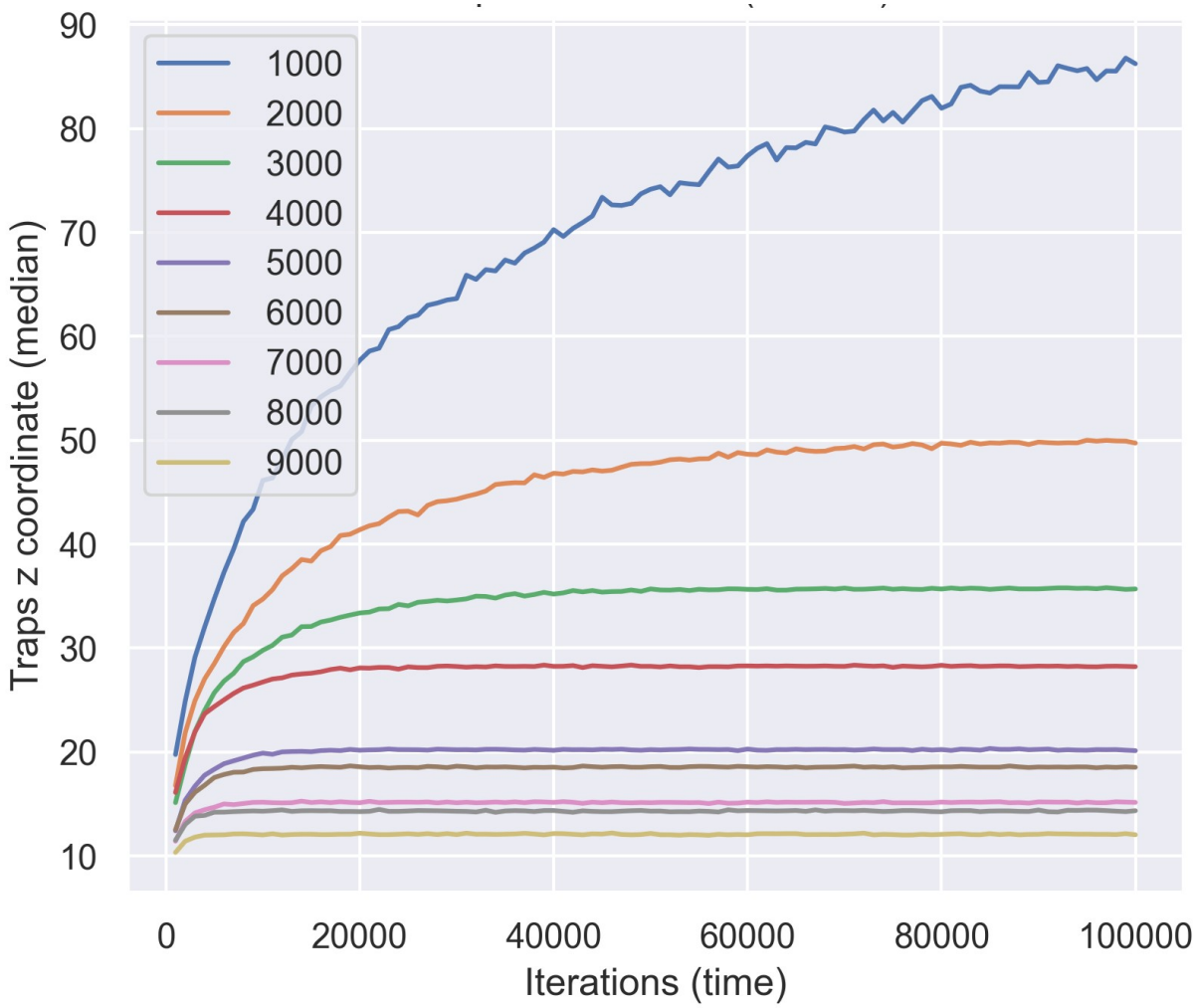

Fig.3. Dynamics of interface, separating the areas with trap filling greater than 50% from the area with less filling, on time (number of iterations) for different trap concentrations

One of the features of the obtained dependences of the interface displacement at different trap concentrations is different. At small number of traps this dependence is slow change on time and may be described as log (t). But at number of traps N_t > 3000 one can observe the asymptotic exit to a plateau at large times. It is possible to explain this behavior due to random placing of traps on the surface of pores these traps are fulfilled enough rapid and as a result the observed plateau.

3.2. The influence of pore size on the time of capture by traps (extinction time)

In this section, we will consider the change in trap capture time - extinction time in pores with different pore radii. Table 2 presents the results of modeling the processes of capture of diffusing particles into traps, namely, determining the extinction time.

Table 2. Results of determining the time of capture by traps (extinction time) with different radius of pores, a is minimal size of problem.

Num	Numb	Num	Numbe	Numb	Numbe	Numbe	Numb	Numb

ber of traps	er of starts N for pore size 3a	ber of steps (iterations) to achieve τ	r of starts N for pore size 9 a	er of steps (iterations) to achieve τ	r of starts N for pore size 27 a	r of steps (iterations) to achieve τ	er of starts N for pore size 81 a	er of steps (iterations) to achieve τ
100	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
110	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
120	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
130	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
140	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
150	18	911475,5	18	889435	11	912947	0	Not achieved
160	3	954140	1	985584	3	956759	0	Not achieved
170	20	863250,5	19	842263	18	876502	0	Not achieved
180	20	797640,5	20	779962	20	811108,5	0	Not achieved
190	20	735504	20	720704	20	742016	7	966902
200	20	768851	19	800765	19	809109	7	963431
210	20	637253	20	633629	20	653986,5	19	859329
220	20	53597	20	550823	20	565895	20	798874

		5						,5
230	20	480339	20	490251	20	531977	20	741447

Table 2 presents the results of modeling the capture of particles by traps in pores of various radii to determine the time of capture by traps (extinction time).

One of the features of results is that with a sufficiently small number of traps N_t <140 for pores with radii R = 3, 9, 27, even at a larger number of steps (iterations) of the order of t =1000,000, it is not possible to achieve a reduction in the number of diffusing particles by 2.7 times and therefore it is impossible to determine the characteristic decrease time when approximating the time dependence of capture by traps with an exponentially decreasing function

It should be noted that an increase in the number of traps N_t > 210 leads to achievements of the extinction time for all sizes according to R = 3, 9, 27, 81, which were used in numerical experiments. Moreover, due to the randomness of the location of traps on the surface and the random movement of particles inside, sometimes there is an exponential decrease in the number of particles immediately upon the first start (first configuration), sometimes later, but on average 20 starts are required, i.e. 20 numerical experiments are required with a given distribution of traps on the surface of the pores. Therefore, the median value of the extinction time across runs was used as the characteristic extinction time at which an exponential decrease in the number of diffusing particles occurs.

The results are presented at Fig. 4.

Figure 4

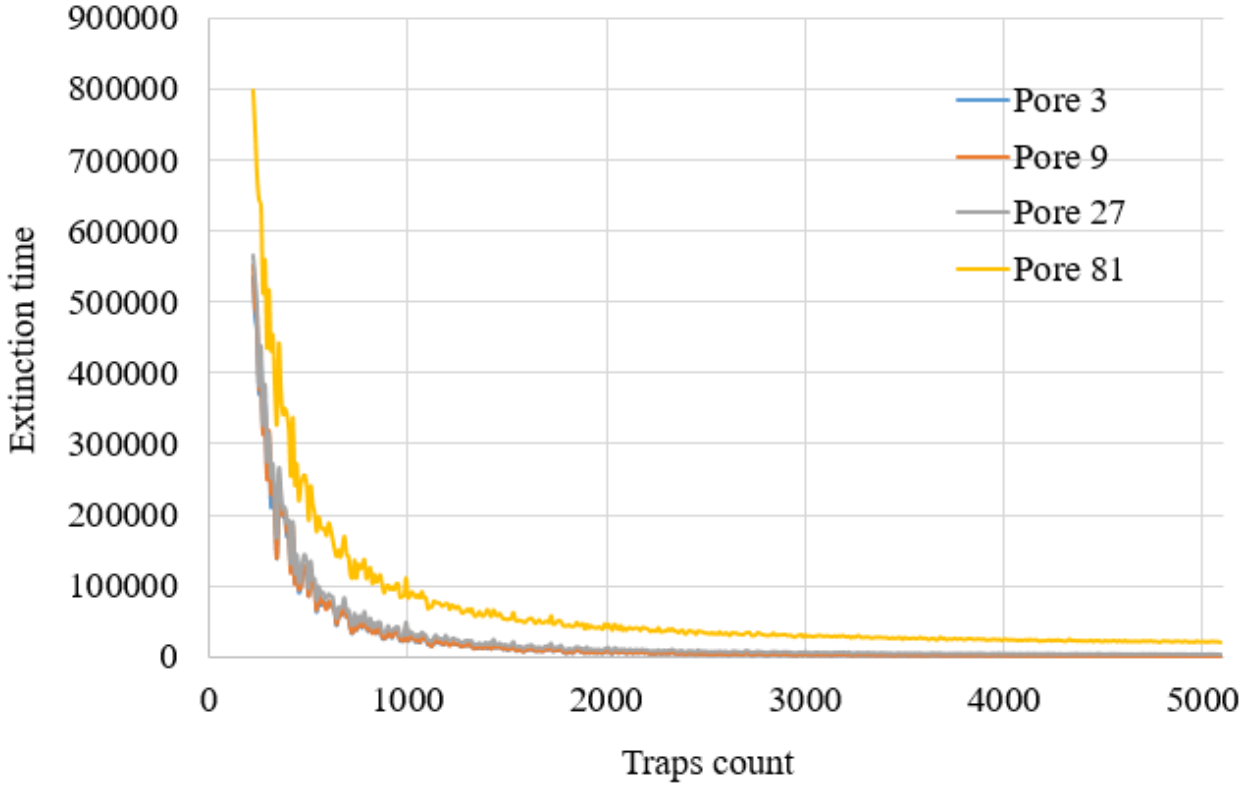

Fig. 4. Dependence of the median capture time on traps (extinction time) on the concentration of traps in pores of radius R=3a, 9a, 27a and R=81a. In

the figure, the x-axis is the number of traps in the experiment, and the y-axis is the extinction time (median value).

A feature of the presented functional dependencies is the general behavior of the capture time on the concentration of traps for pores with radii R=3a, 9a, 27a and significantly different behavior for a pore with a radius R=81a. For a more complete and thorough analysis of the functional nature of the change in capture time, we will divide the intervals with a small number of traps N_t <1000 and with a large number of traps N_t > 1000 - see Fig.5a

Figure 5a

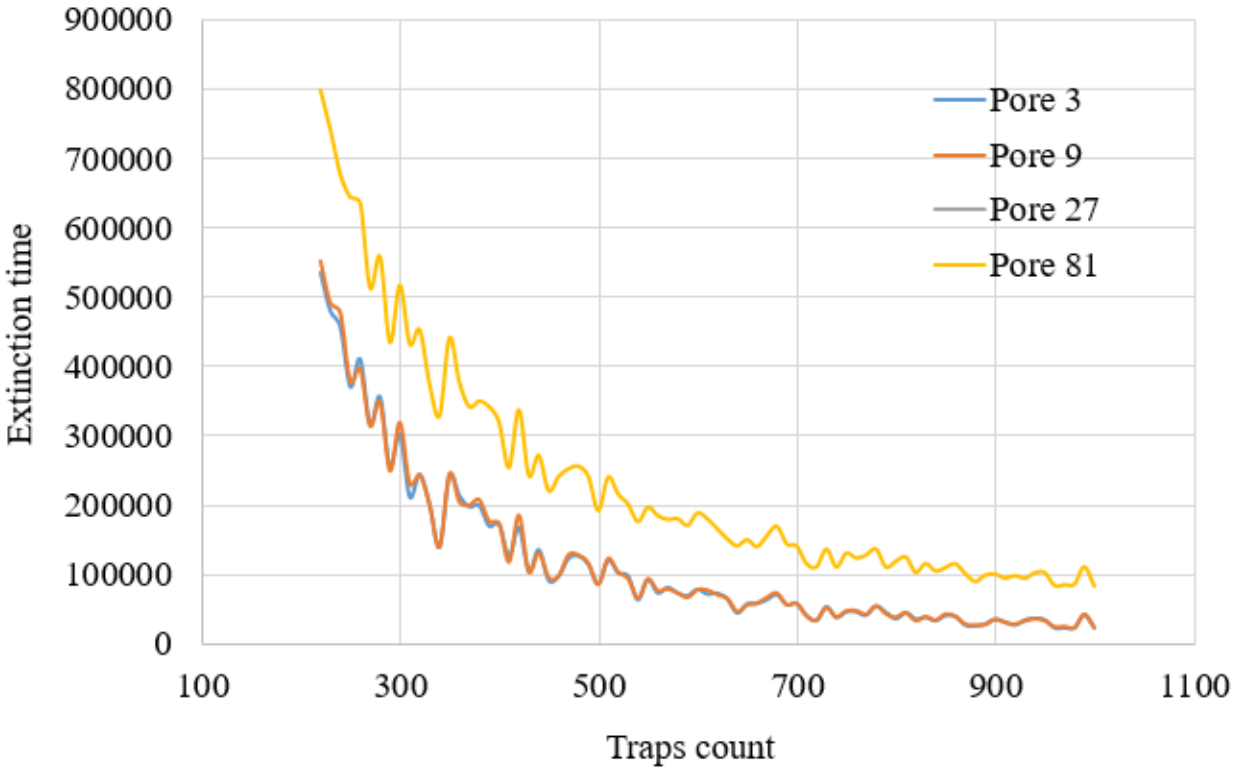

Fig. 5a) Dependence of capture time on traps (extinction time) on the number of traps
inside pores with different radii and a small number of traps Nt <1000.

For small numbers of traps, the functional dependences of the decrease are of a similar nature: for pores with a radius R = 3a, 9a, 27a they actually coincide, but for a pore with a radius R = 81a the decrease is slower. This can be easily verified by renormalizing the coordinates for a pore with a radius of R= 81a - see Fig. 5b)

Figure 5b

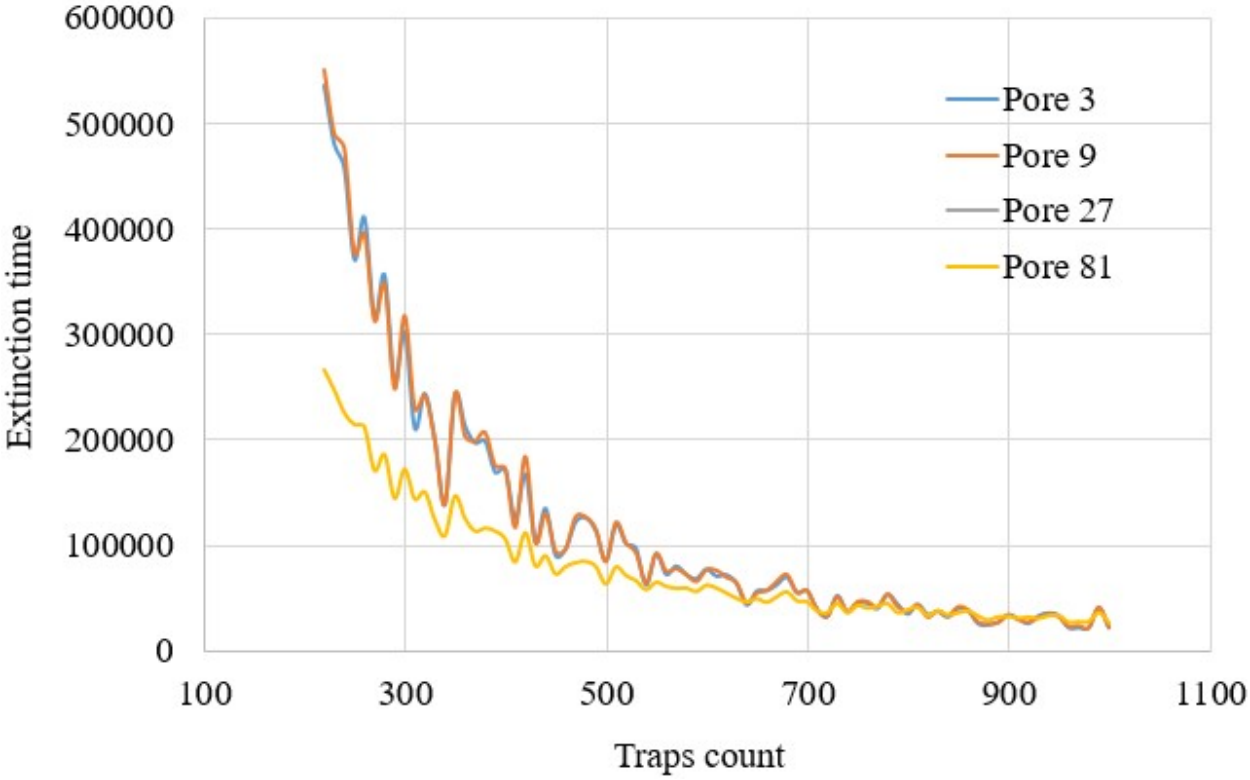

Fig. 5b) Dependence of capture time on traps (extinction time) on the number of traps
inside pores with different radii and a small number of traps Nt <1000. The value for a pore with radius R=81a is reduced by 3 times.

A feature of the obtained functional dependencies is a slower decrease for the case of a pore with a radius R = 81a, which is due to the need for particles to diffuse over much greater distances to get into traps. Another unexpected feature is the apparently different functional dependence on the number of traps. Further research is required to establish this relationship.

Figure 5c

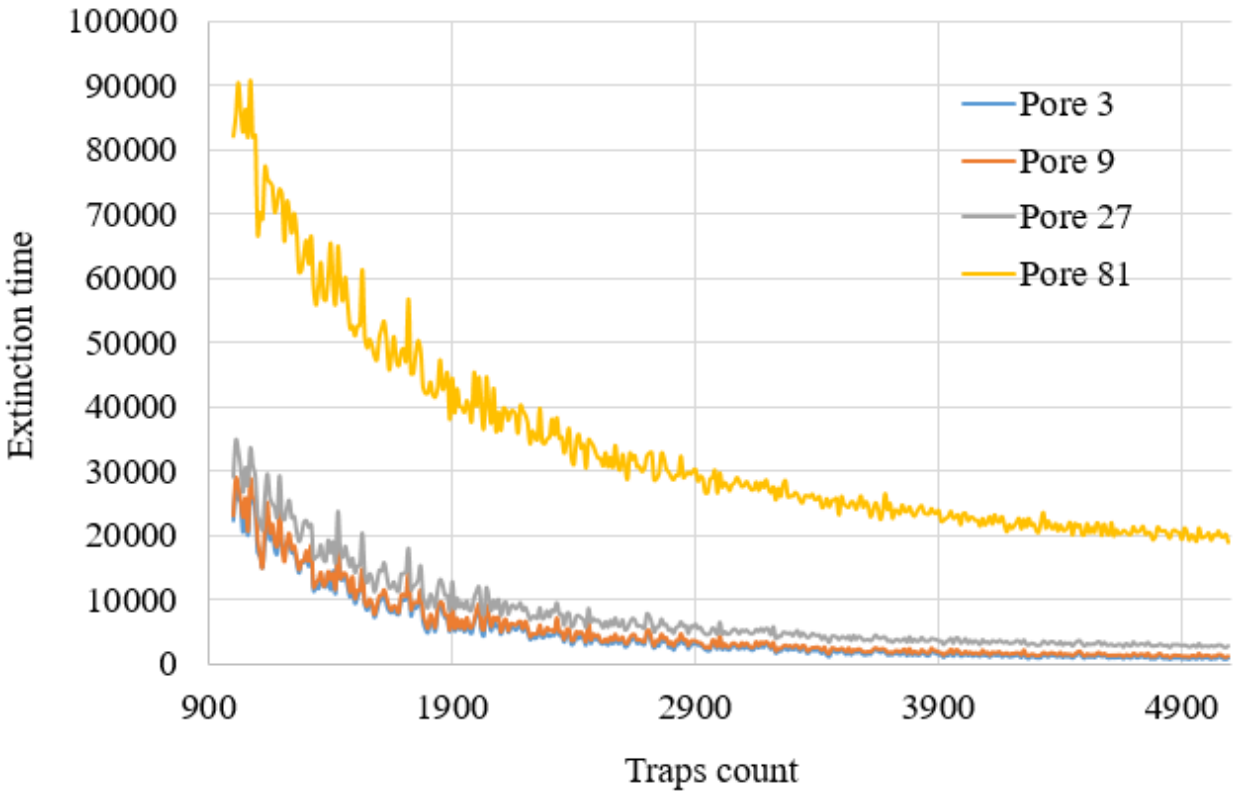

Fig. 5c) Dependence of capture time on traps (extinction time) on the number of traps
inside pores with different radii with a large number of traps Nt > 1000.

Here we can also see a different functional dependence of the time of capture by traps (extinction time) for pores with a radius of 81 a, in contrast to the behavior for pores with a radius of R=3 a, R=9 a, R= 27 a.
Thus, the capture by traps in pores turns out to be significantly different depending on both the size of the pore radius and the number of traps. We will discuss the physical reasons for this in the Conclusion.

Also, to check the reliability of the data obtained, an estimate of the normality of the distribution of standard deviations for the values of extinction times was obtained - see Appendix A

5. CONCLUSIONS

Numerical modeling of particle capture by traps in cylindrical pores of material was carried out. Different behavior of the time dependences of the number of active particles at small times $t<<t_c$ and at large times $t>>t_c$ has been established; the characteristic time t_c is the time of capture by traps. Over the interval up to times t_c, a rapid exponential decrease in the number of active particles due to capture by traps has been established as it is expected, however, at asymptotically large times, strong fluctuations in the change in the number of active particles are observed. An unusual step-like behavior of the temporal asymptotic of the number of active particles was discovered; this can be explained by the appearance on the cylindrical surface of regions free of traps and appeared due to fluctuations in the

concentration of traps. The statistics of these fluctuation regions has been studied.

The dynamics of the boundary separating regions with trap filling greater than 50% from the region with less filling with time (number of iterations) for different trap concentrations was studied in detail. It has been established that at longer times the movement of the boundary slows down and reaches a plateau. In our opinion, the possible emergence of a plateau at large times are connected with fast fulfilling the 50% of traps and further the low fulfilling because the free traps are placed at large distances from the edge of pore structure and there are big times to reach these free traps, but further studies of these processes are necessary.

The influence of pore radius for a capture on traps, placed on the internal surface pore was studied. According our results the capture on the traps, placed on internal surface of pores, is similar for pores with radius R=3 a, R=9 a, 27a and is differ for pore with R=81 a. It is possible to explain that space for a diffusing particles for pores with small radius is confined and the capture of particles is enough often occur, but in the case of pore with big radius the particles reach the surface in a rare way and the process of capture is slow due to this fact.

Also the processes of capture is different for different number of traps. In the case of small number of traps less than 1000 – Fig. 5a the value of time of trap capture is change for 10 times for pores with R=3-27 a and change only for 5 times at R=81 a. But for a case number of traps more than 1000 – Fig. 5c) the value of extinction time for pore R=81 is change for approximately 5 b times, but for pores with radius R= 3 -27 a is going to small value at number of traps 5000. So it is show that the capture on traps inside pores depends on the radius of pores of materials.

These results are important for an understanding of influence of geometry of pores for the process of penetration of particles and capture of on traps in the pores with random form. For example, if the pores have different radius along axis of cylinder pores as one can see at Fig.6, so the process of capture on traps in the pores with variable radius and temporal asymptotic of survival probability of particles will be determined «narrow neck». In the case of consequent connection of pores the effective time will be determined the characteristic time of this «narrow neck». According our results the difference of extinction time is appeared when difference between values of radius became big enough.

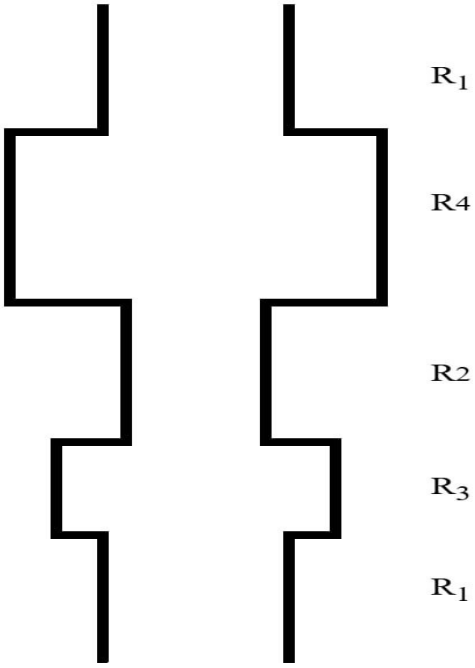

Fig. 6. Pore with variable radius

In the case of branched pores with different radius when there is a possibility to escape the «narrow neck» may be the percolation approach will be useful to determine the effective extinction time for pore with complex branched structure. Further investigations are necessary to clear the issue with branched structure of pores.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Appendix A The estimation of standard deviation for extinction times.
To check the data, the normality of the distribution of standard deviations for extinction times for different pore radii was assessed. The results of estimations are presented at Fig 6a) and Fig 6b)

Figure 6a

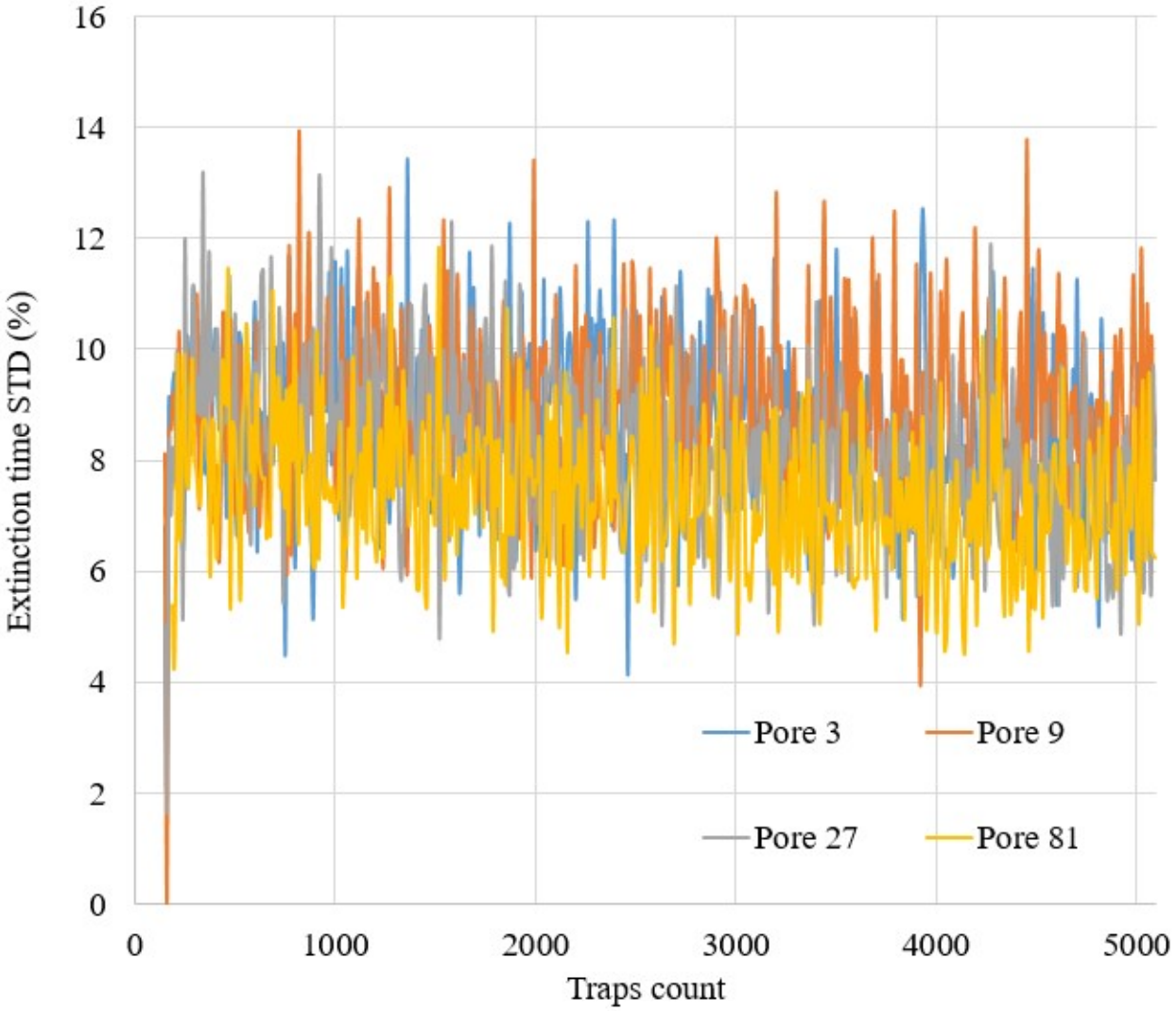

Fig 6a). The standard deviation for pores with different radius, which presented different colous

Because the time of capture for all starts is reached for configurations with number of traps N_t >200 so the graph is begins from this value. The value of mean standard deviation is change from 4% to 14% with the same random dependency for all pores.

Figure 6b

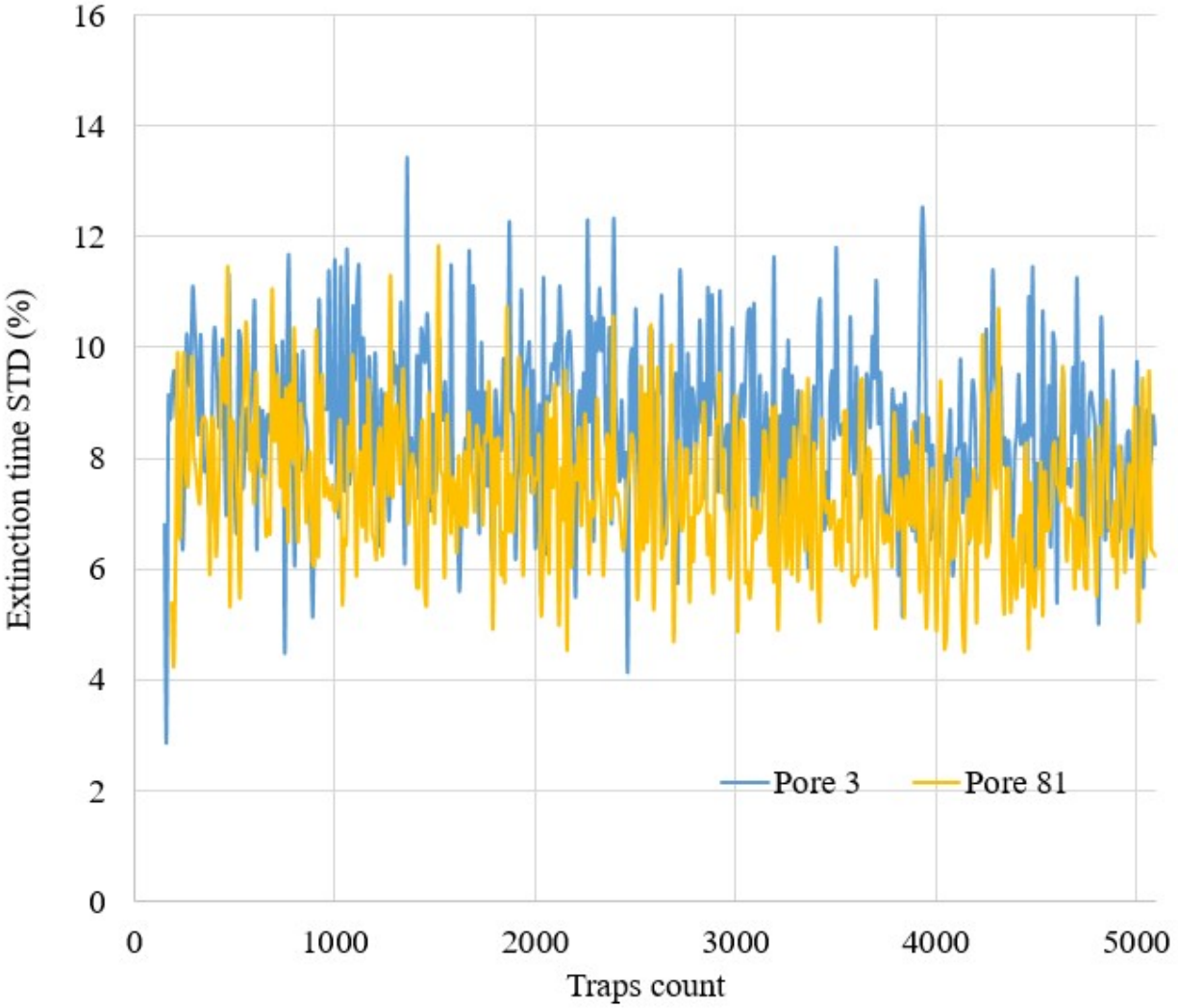

Fig. 6b) The standard deviation for a case with radius pore R=3 a and R=81 a

After checking on can say that this standard deviation is corresponded to normal distribution of errors.

TABLES

Table 1. The average and median value of the z coordinate for closed traps (configuration with the number of traps 1000)

№	Number of steps (number of iterations)	Median value	Mean value
1	1000	23,4	21,705
2	5000	32,0	36,494
3	10000	43,0	46,680
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9	70000	75,0	74,556
10	80000	81,0	81,934
11	90000	85,5	84,524

12	100000	88,5	89,394

Table 2. Results of determining the time of capture by traps (extinction time) with different radius of pores, a is minimal size of problem.

Number of traps	Number of starts N for pore size 3a	Number of steps (iterations) to achieve τ	Number of starts N for pore size 9 a	Number of steps (iterations) to achieve τ	Number of starts N for pore size 27 a	Number of steps (iterations) to achieve τ	Number of starts N for pore size 81 a	Number of steps (iterations) to achieve τ
100	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
110	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
120	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
130	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
140	0	Not achieved	0	Not achieved	0	Not achieved	0	Not achieved
150	18	911475,5	18	889435	11	912947	0	Not achieved
160	3	954140	1	985584	3	956759	0	Not achieved
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Figure 1

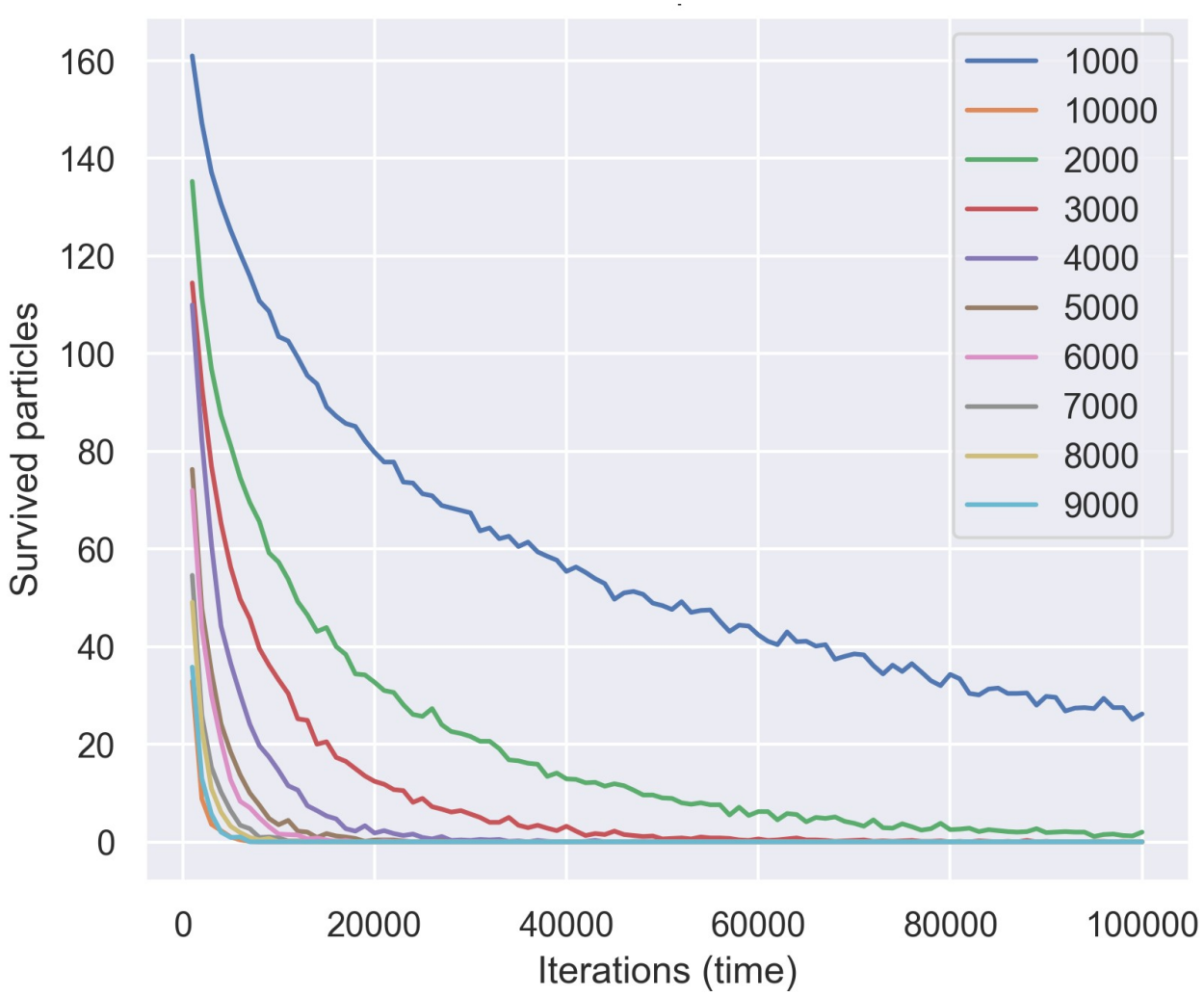

Figure 2

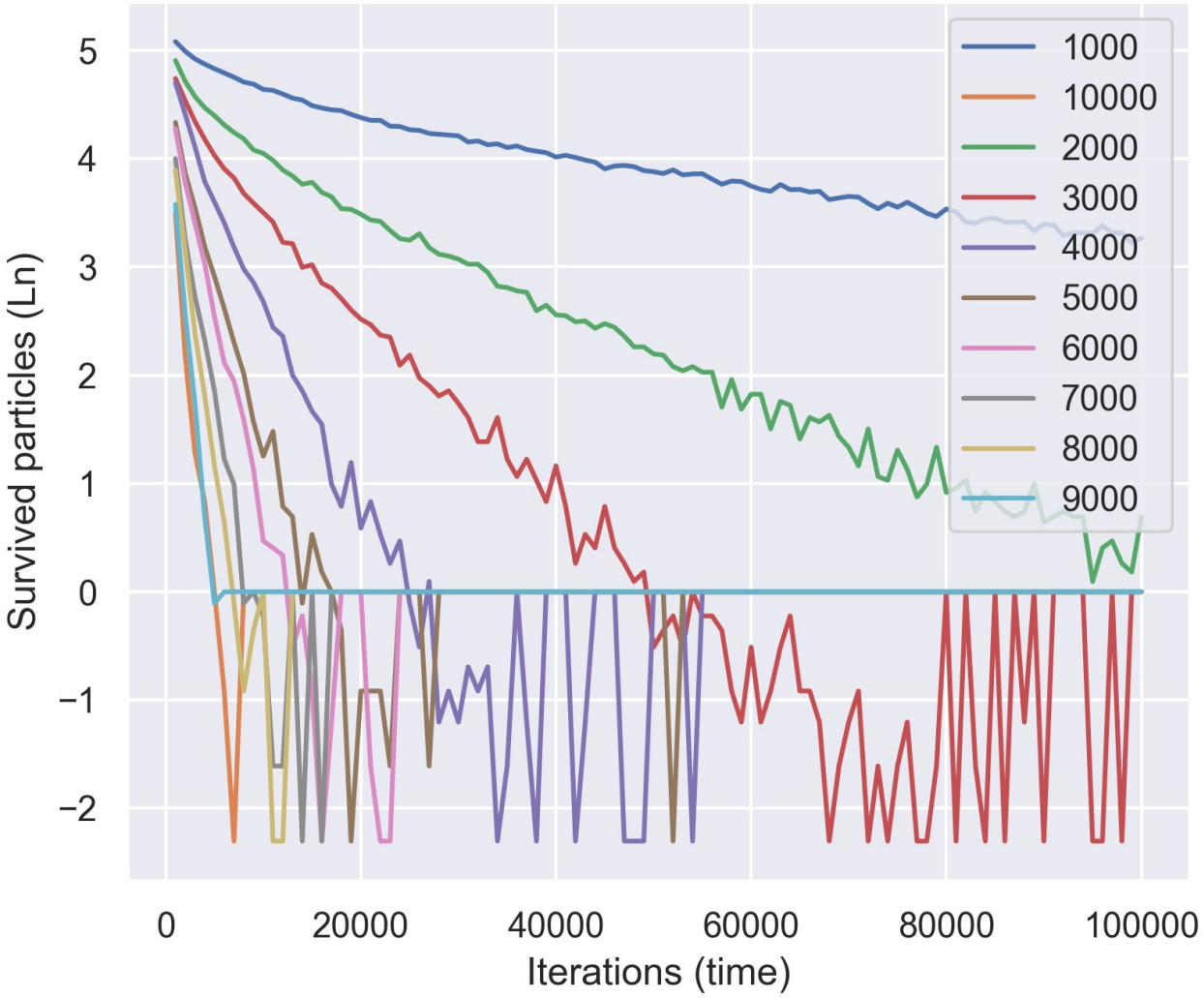
Survived particles (Ln)
5
4
3
2
1
0
−1
−2
0
20000
40000
60000
80000
100000
Iterations (time)
1000
10000
2000
3000
4000
5000
6000
7000
8000
9000

Figure 3

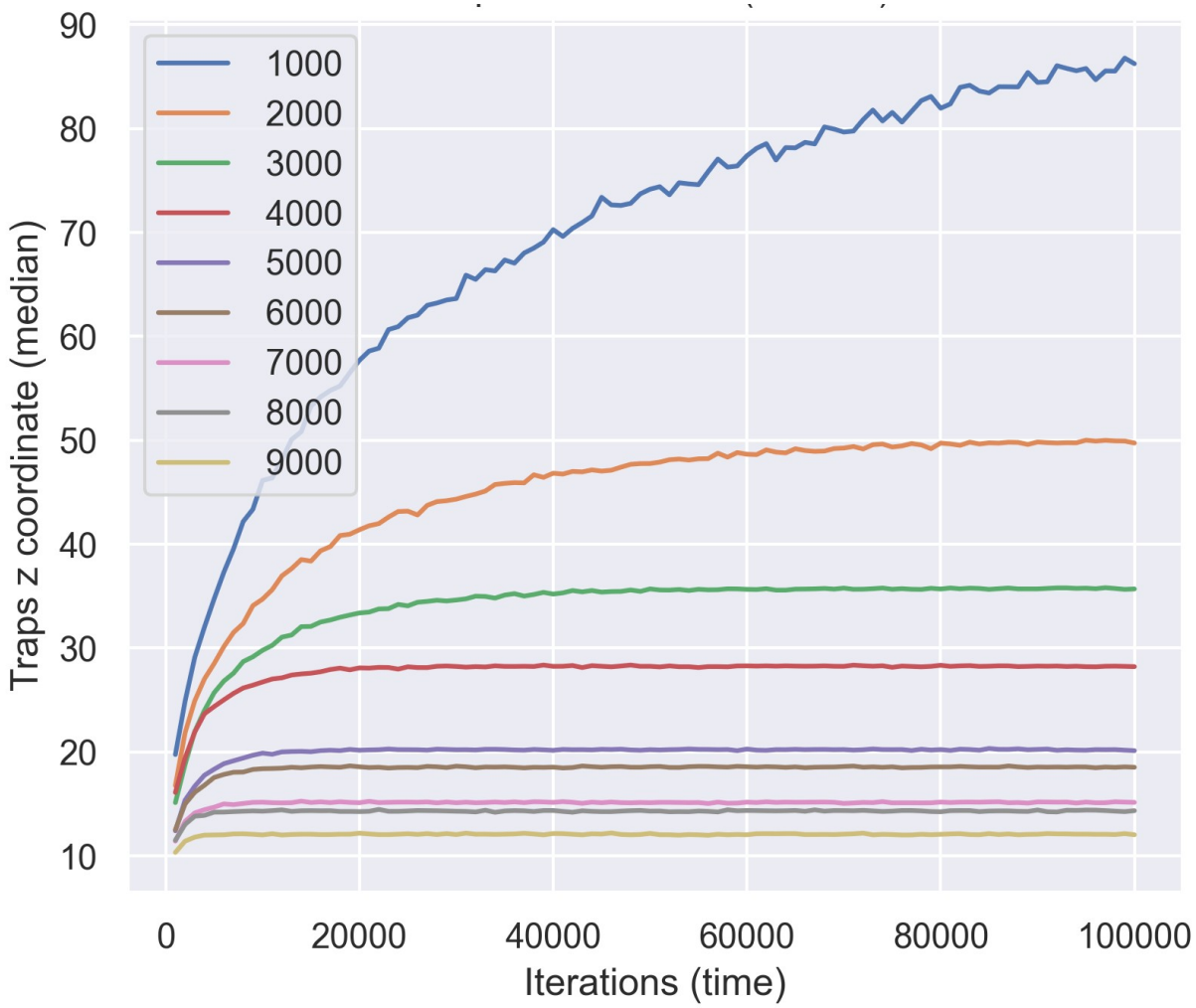
1000
2000
3000
4000
5000
6000
7000
8000
9000
Traps z coordinate (median)
Iterations (time)
90
80
70
60
50
40
30
20
10
0
20000
40000
60000
80000
100000

Figure 4

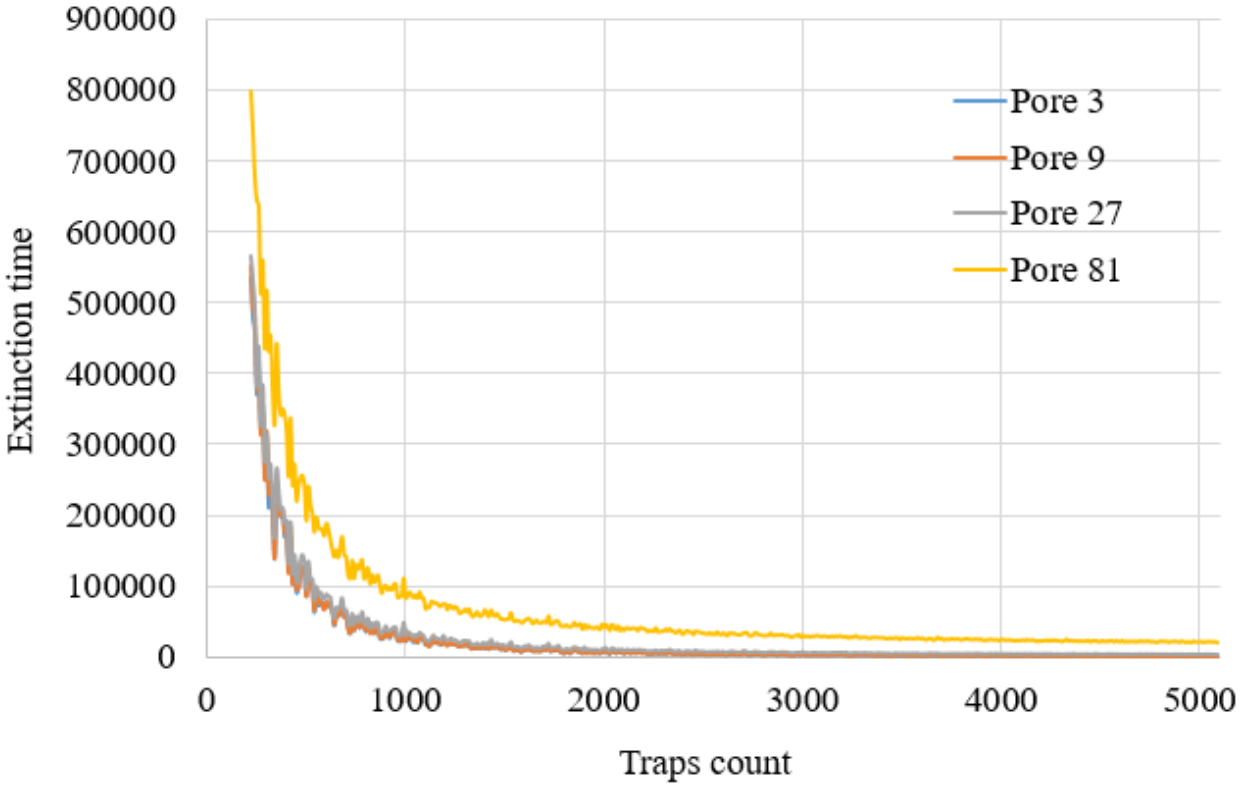

Figure 5 a

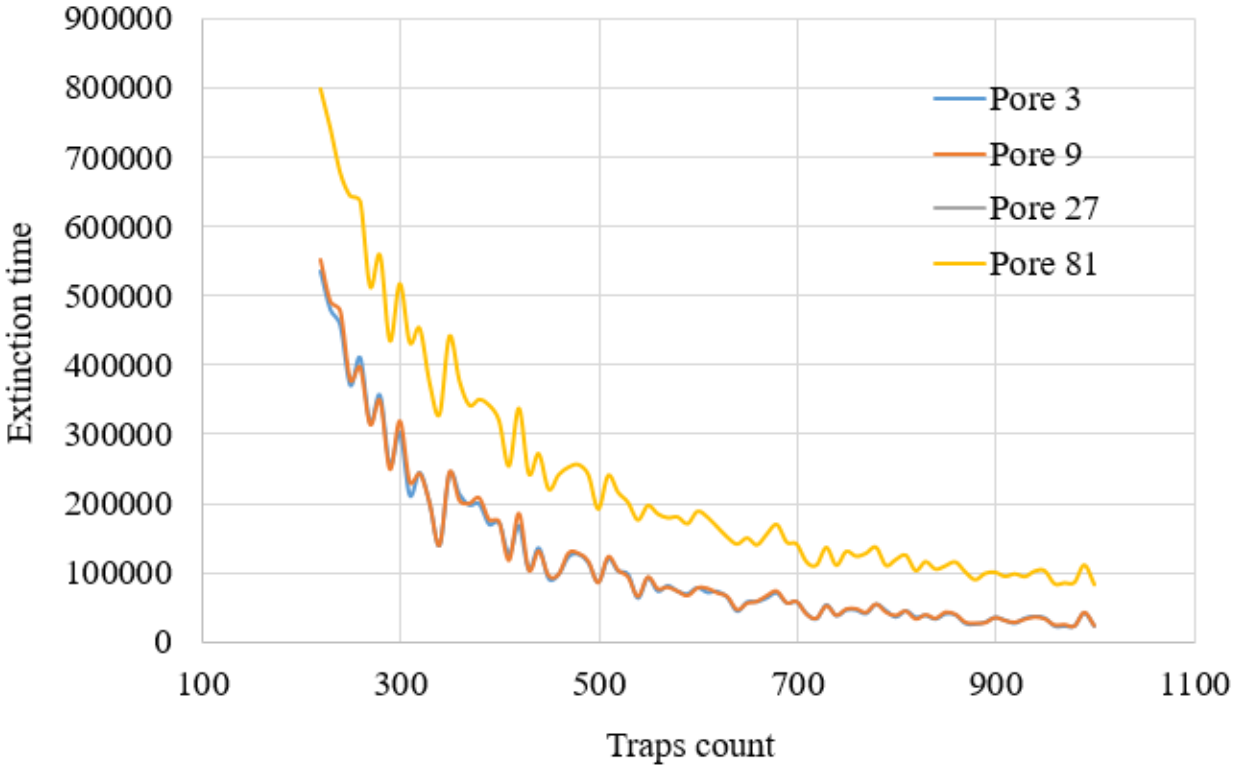

Figure 5 b

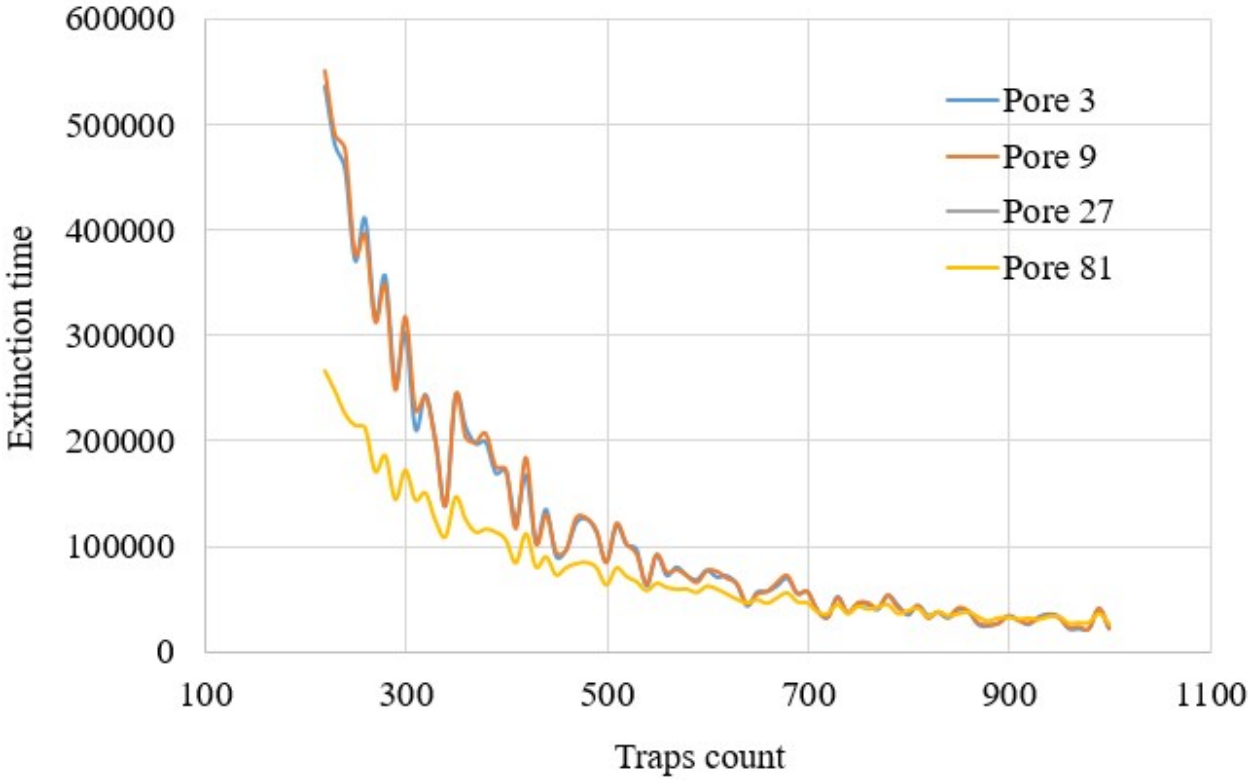

Figure 5 c

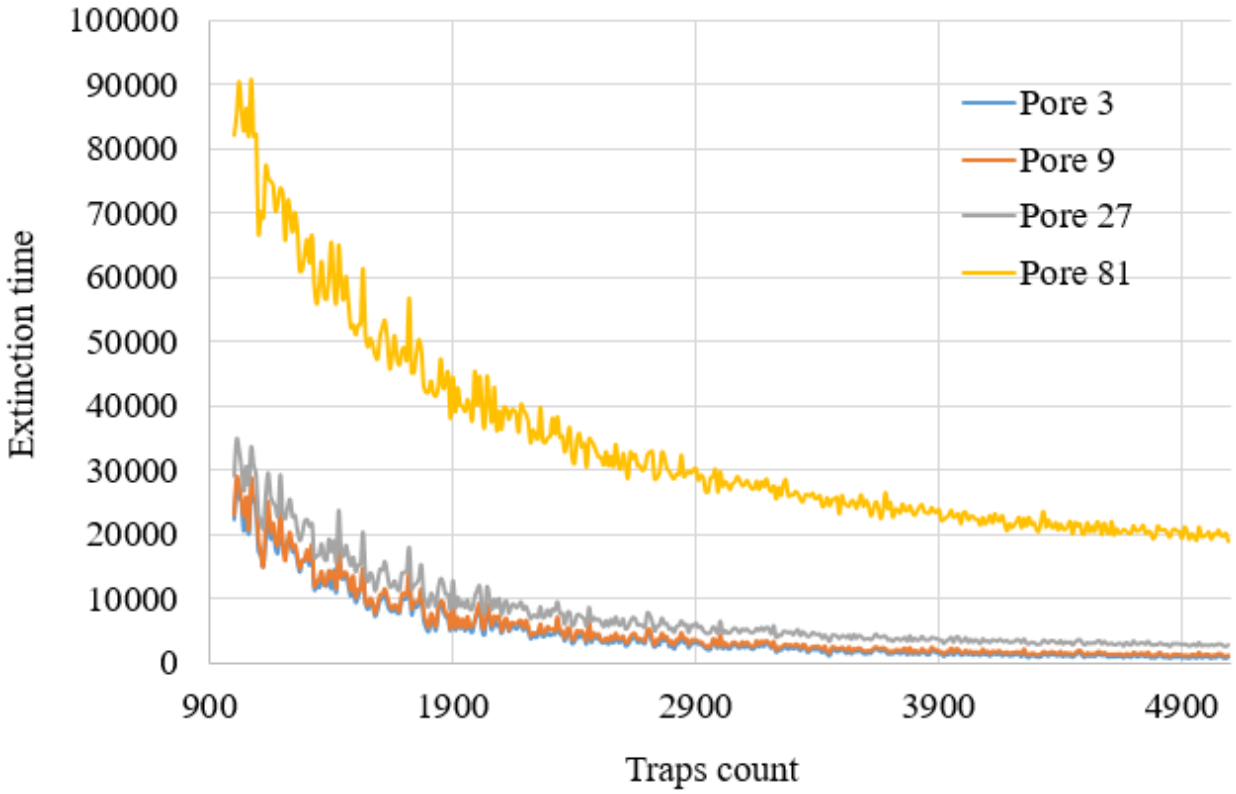

Figure 6 a

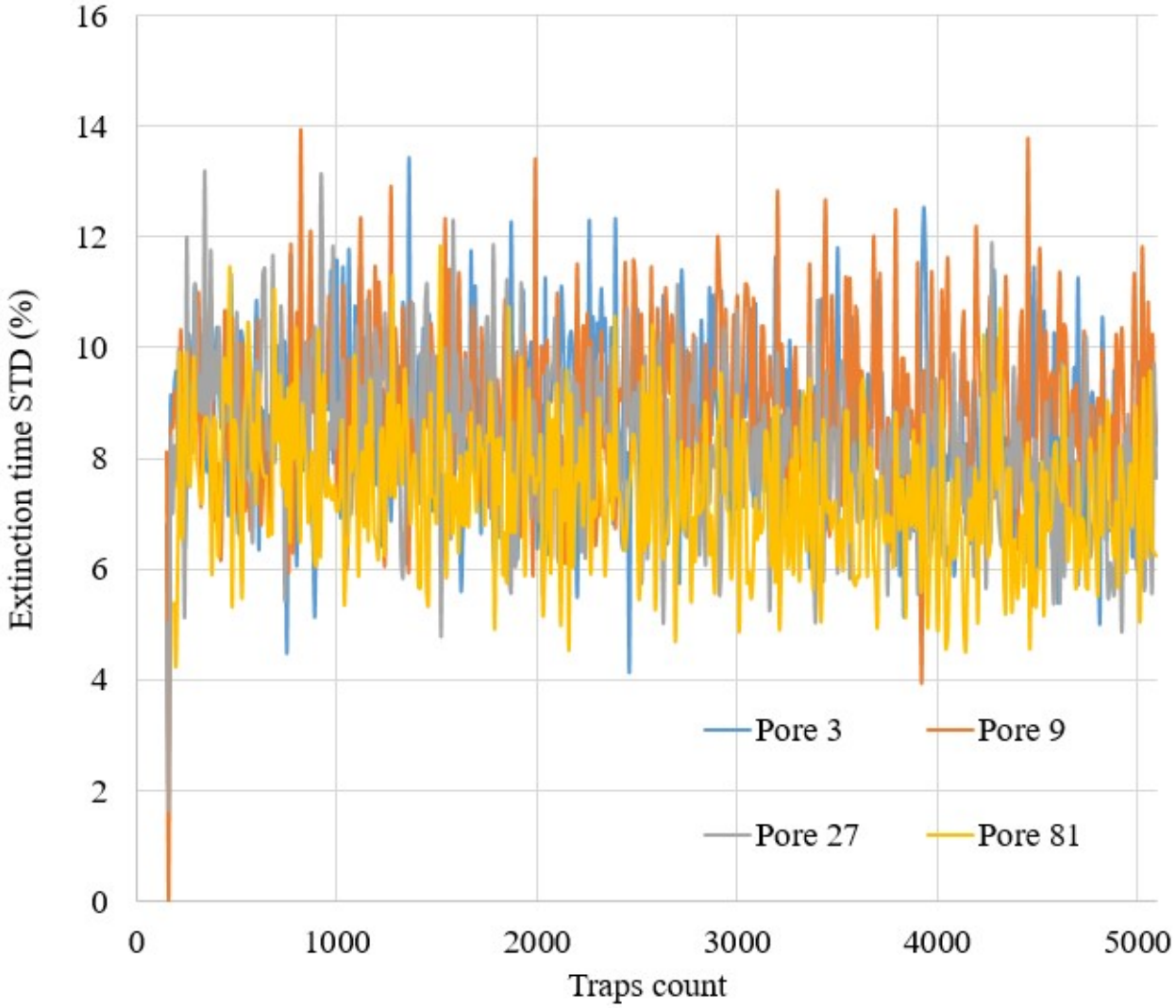
16
14
12
10
8
6
4
2
0
Extinction time STD (%)
0
1000
2000
3000
4000
5000
Traps count
Pore 3
Pore 9
Pore 27
Pore 81

Figure 6 b

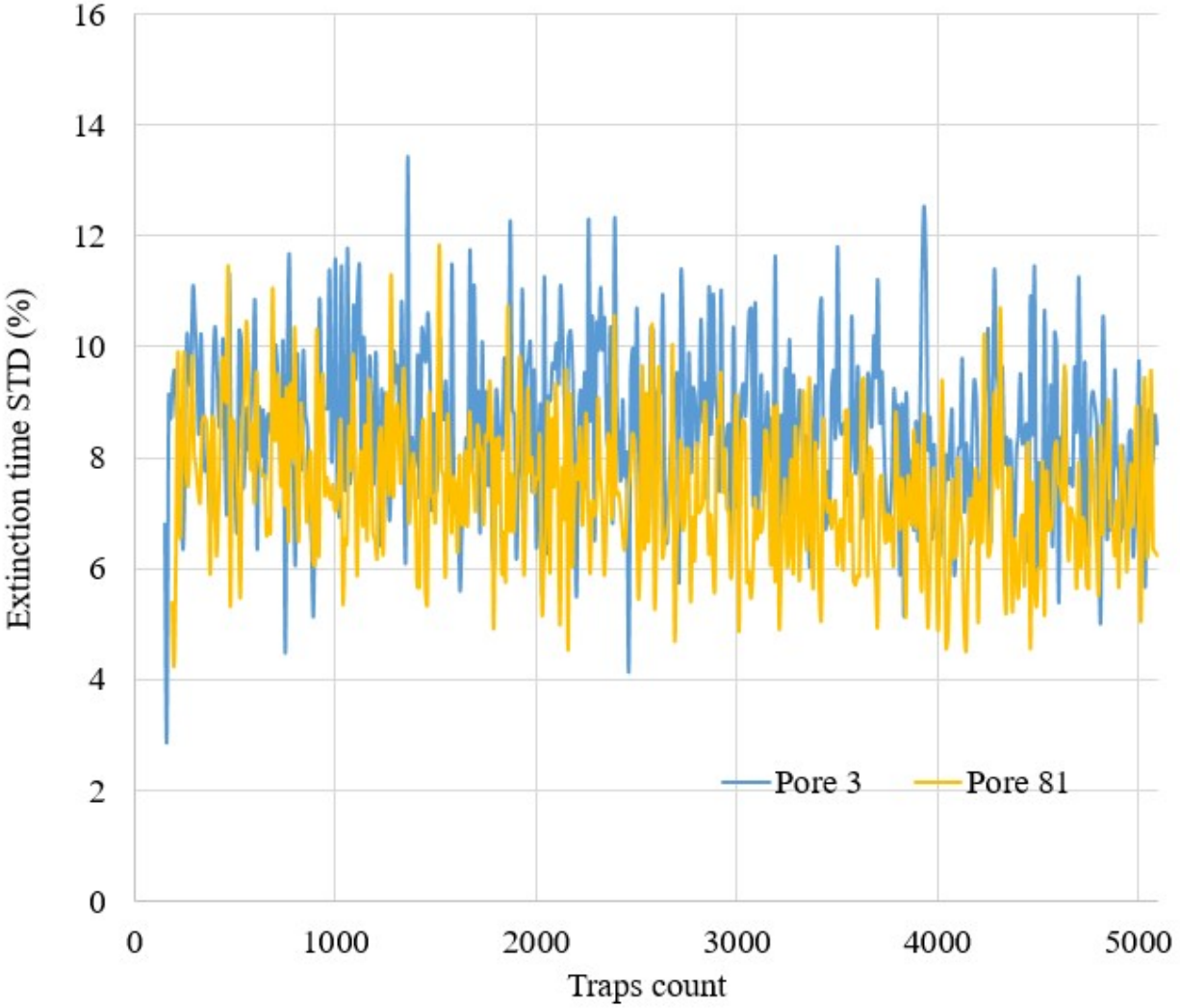

Fig.1 Dependence of number of survived particles on the time (iterations) at different number of traps.

Fig.2. Dependence of logarithm of number of active particles on time at different concentrations of traps.

Fig.3. Dynamics of interface, separating the areas with trap filling greater than 50% from the area with less filling, on time (number of iterations) for different trap concentrations

Fig. 4. Dependence of the median capture time on traps (extinction time) on the concentration of traps in pores of radius R=3a, 9a, 27a and R=81a. In the figure, the x-axis is the number of traps in the experiment, and the y-axis is the extinction time (median value).

Fig. 5a) Dependence of capture time on traps (extinction time) on the number of traps
inside pores with different radii and a small number of traps Nt <1000.

Fig. 5b) Dependence of capture time on traps (extinction time) on the number of traps
inside pores with different radii and a small number of traps Nt <1000. The value for a pore with radius R=81a is reduced by 3 times.

Fig. 5c) Dependence of capture time on traps (extinction time) on the number of traps

inside pores with different radii with a large number of traps Nt > 1000.
Fig. 6a). The standard deviation for pores with different radius, which presented different colors
Fig. 6b) The standard deviation for a case with radius pore R=3 a and R=81 a